

GASEOUS EXPLOSIONS

**Initial Temperature and Rate of
Rise of Pressure**

GEORGE GRANGER BROWN

**A Thesis submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy in the
University of Michigan**

ANN ARBOR

1924



Pure Hydrocarbons from Petroleum¹

By G. G. Brown and A. R. Carr

UNIVERSITY OF MICHIGAN, ANN ARBOR, MICH.

COMMERCIAL straight-run gasoline from the Cabin Creek Field was systematically fractionated in a column, 18 feet high, packed with modified Raschig rings $\frac{1}{2}$ inch in diameter, in a similar column 10 feet high containing $\frac{1}{4}$ -inch rings, and in a glass column 5 feet high packed with $\frac{1}{8}$ -inch rings. Five fractionations were sufficient to separate cyclopentane, cyclohexane, benzene, and toluene from the pentanes and hexanes and gave 200 cc. of isopentane (30.5° to 30.6° C.) and 250 cc. of normal pentane (36.2° to 36.3° C.). Seven fractionations gave 300 cc. of isohexane (61.1° to 61.2° C.) and 1000 cc. of normal hexane (68.9° to 69.0° C.). Nine fractionations separated 2000 cc. of normal heptane (98.6° C. to 98.7° C.). Ten fractionations gave 2500 cc. of isoöctane (117.9° to 118.1° C.), 1100 cc. of normal octane (124.3° to 124.5° C.) and 600 cc. of normal nonane (150.2° to 150.9° C.).

This work with imperfect columns of moderate efficiency indicates that pure hydrocarbons of boiling points up to 150° C. may be obtained by systematic fractionation at atmospheric pressure.

APPARENTLY, no previous attempt to obtain appreciable quantities of pure hydrocarbons by systematic fractional distillation of petroleum has been reported. Many attempts to identify the hydrocarbons in petroleum are recorded, and the basis of all methods employed has been separation by distillation. Usually only simple distillation has been used. In only rare instances has a fractionating column of any kind been adopted.

As the purpose was to produce pure hydrocarbons to be used for purposes of research, and not simply to isolate small quantities for the purpose of identification, the use of an efficient type of fractionating apparatus was imperative.

Historical

The simple stills used by Pelouze and Cahours,^{1,*} Schorlemmer,² Beilstein and Kurbatow,³ and Mabery⁴ in separating

¹ Received March 1, 1926. Presented before the Division of Petroleum Chemistry at the 71st Meeting of the American Chemical Society, Tulsa, Okla., April 5 to 9, 1926.

* Numbers in text refer to bibliography at end of article.

the hydrocarbons for purposes of identification gave very unsatisfactory results. The use of Engler flasks^{5,6,7} led Coates⁸ to state:

It is exceedingly difficult to get the hydrocarbons in a state of purity. Indeed, I do not think it can be done by distillation. Several hundred distillations were made, but each fraction continued to break up into fractions with lower and higher boiling points.

Warren⁹ introduced the use of a fractional condenser or dephlegmator composed of a worm surrounded by a bath whose temperature could be controlled. This equipment was also used by Mabery,⁴ who found it more effective than the Hempel column, although demanding more attention. Young and Thomas¹⁰ used a similar dephlegmator described as a "regulated temperature stillhead" in conjunction with a pear column.¹¹ With this equipment they were able to separate the pentanes from the butanes in one distillation and to separate the pentanes from each other in twelve distillations.

Bushong¹² used a copper retort and glass flasks equipped with a Le Bel-Henninger dephlegmator. The hydrocarbons were heated directly by a coil of German silver wire within the flask. Fractions were cut every 2° C. Bushong makes the interesting statement that he "is firmly convinced that a series of fractional distillations carried out on a factory scale would richly reward the immense labor involved by opening up a new world of possibilities in the way of chemical products to be manufactured from petroleum."

Evans¹³ conducted a distillation of the light fractions of Asiatic petroleum, using three different columns, first a Young's 12-bulb pear column, then a 75-cm. glass column containing lead balls 5 mm. in diameter, and finally though a 75-cm. column containing at the lower end 10 cm. of copper gauze, then 30 cm. of steel balls 2 mm. in diameter, and the upper 35 cm. filled with steel balls 4 mm. in diameter. The third column was found to be the best.

Reed and Williams¹⁴ distilled crude oil from a long-neck, round-bottom flask. The fraction up to 170° C. so obtained was then distilled from a similar flask through a 4-pear stillhead. The column was 58 cm. high and the bulbs were 2.5 cm. The rate of distillation was 2 drops a second. A similar 102-cm. column containing 8 pears was used to distil the fraction under 180° C. at the same rate. Cuts were made at 30° C. intervals.

Anderson and Erskine¹⁵ identified the compounds present in natural gas gasoline by distillation in "ordinary columns" and with "a regulated temperature stillhead." With this procedure eight fractionations were sufficient to separate the pentanes into fractions boiling within 0.5° C., nine fractionations separated the hexanes into 1.0° C. fractions, and seventeen fractionations separated the heptanes into 1.0° C.

fractions. These results, rather unsatisfactory in themselves, are the best of any so far recorded.

Fractionating Column the Best Means

From the experience briefly reviewed above it is evident that efficient fractionation of petroleum can be accomplished only by means of a column. This fact can be theoretically deduced by the method given by Leslie,¹⁶ who shows that the ideal fractionating column is always more efficient than either the ideal simple dephlegmator or differential dephlegmator for making complete separations into pure components, or by a careful consideration of the fundamentals of distillation.

The ideal distillation process at constant pressure consists in countercurrently contacting the upward flowing vapor and the downward flowing liquid so intimately that equilibrium is established at all points and the change in composition of the phases occurs continuously. The dephlegmator is a partial condenser operated to serve the double purpose of refluxing or returning part of the distillate to the still and washing the rising vapors with this refluxed liquid. In an apparatus of this kind condensation takes place throughout its entire length. A large part of the condensed liquid is formed in the lower parts of the dephlegmator and returns to the still, traversing only a small part of the total length of the apparatus. The same total effective washing could be attained by condensing a much smaller quantity of liquid if it were all returned from the extreme end of the apparatus as is done in the fractionating column. These considerations indicate that the column should be as nearly adiabatic as possible, the heat loss being entirely in the condenser and reflux.

Preliminary Tests of Fractionating Columns

The first column constructed was similar to the column described by Dufton,¹⁷ who reported that this type was very satisfactory for distilling small amounts of liquids as the amount of liquid contained in the column was a minimum. The column was made of an 8-foot length of 4-inch iron pipe with standard cast-iron flanges on either end. It contained a helix wound around a closed core constructed of a 2-foot length of 2-inch pipe welded to a 3-foot length of 2 $\frac{1}{4}$ -inch pipe topped by 2 feet 8 inches of a 2 $\frac{1}{2}$ -inch pipe. The helix was welded to the core, 1 $\frac{1}{2}$ inches between turns, and closely fitted the inside of the column. The column was bolted to the still through a special iron gasket used as the support of the helix core. The still body was made of welded $\frac{1}{4}$ -inch steel plate of about 15 gallons capacity. A look box was provided on top of the column so that the amount of reflux could be observed. The total condenser was made by forming a 20-foot length of 1-inch iron pipe into a coil 1 foot inside diameter and immersed in water, or ice and water, as the occasion demanded.

The liquid in the still was heated internally by a coil of chromel "A" resistance wire. The coil was mounted on a wooden platform made fast to the cover of the hand hole. Contact was made through two porcelain spark plugs in the hand hole cover. Current was taken from a 220-volt direct current line and controlled by means of a rheostat of the granular resistance type. The still and column were lagged with 85 per cent magnesia about 2 inches thick. Preliminary work on the separation of benzene-toluene mixtures in this column gave very unsatisfactory results.

The helix was removed and the column was filled with modified Raschig rings $\frac{1}{2}$ inch in diameter. This type of packing provided a greater countercurrent contacting surface and free volume than the helix. These rings were made from sheet metal cut to the proper length and width and formed in a mandrel. Preliminary work with this second column also gave unsatisfactory results, although much better than the first column.

The length of the column was then increased by adding a 10-foot length of 3-inch pipe above the 8 feet of 4-inch pipe. This 18-foot column was filled with the same Raschig rings separated by the insertion of truncated cones of perforated sheet metal, every 2 feet. These cones served the purpose of directing the downward flowing liquid toward the center of the column, as it had been noticed that the returning liquid had a tendency to flow down the inside walls.

Preliminary work on the separation of benzene-toluene mixtures in this 28-foot column gave satisfactory results. The intermediate fraction was fairly constant, containing about 2 liters regardless of the amount of liquid distilled.

Gasoline Used

One hundred and thirty-five gallons of straight-run gasoline distilled from crude oil from the Cabin Creek Field, W. Va., were obtained from the Elk Refining Co., Charleston, W. Va. The A. S. T. M. distillation of this gasoline ran as follows:

Per cent	° F.	° C.	Per cent	° F.	° C.
Initial	144	42.2			
10	196	91.1	70	280	138
20	215	101.7	80	297	146.9
30	229	109.4	90	321	160.5
40	243	117.8	95	344	173.5
50	257	124.9	(end) 98.5	376	191.4
60	268	131.5	Specific gravity 0.7260 at 21°/15° C.		

Two samples tested for sulfur by the "doctor" tests gave negative results; five samples tested by the more thorough lead acetate and sodium nitroprussiate test also gave negative results for sulfur. Six samples tested for nitrogen by treatment with sodium and a ferrous salt gave no ferrocyanide test, showing the absence of nitrogen. The results of two checks in combustion tests gave 86.16 per cent carbon and 13.43 per cent hydrogen. From these tests we may assume that the gasoline used was a mixture of pure hydrocarbons.

Preliminary Distillation of Gasoline

In distilling gasoline it was found that the heavy residue remaining in the still after the lighter fractions had been taken off was at so high a temperature that gasoline could not be charged directly into the still until after it had been cooled for 3 to 5 hours, because the highly volatile components of the fresh charge would vaporize and create such pressures as to prevent the liquid from running into the still body. As this work was conducted, not as an end in itself, but simply to supply raw material for further study, results had to be obtained in the shortest possible time. Accordingly, the still was equipped with a 10-gallon blow case in order to charge the still promptly and not lose time, as the work was carried out on the shift basis, operating 24 hours a day.

The air was supplied by a hand-operated diaphragm pump. A gage glass was so arranged that the flow of liquid into the still could be observed and the cock closed promptly to prevent an excess of air from entering the still.

Because of the limited capacity of the still it was impossible to fractionate the entire quantity of gasoline in one run. So the still was filled, run down as far as possible, and refilled by raw gasoline. This process was continued until the heavy residue in the still amounted to 5 gallons, when it was drained and another similar run was made.

At the end of three runs of this kind all of the gasoline had been distilled once and collected into the following fractions:

Temperature		Weight	
° C.	° F.	Kgs.	Lbs.
Below 55	Below 131	2.5	5.5
55 to 90	131 to 194	82.5	181.75
90 to 110	194 to 230	57	124.75
110 to 120	230 to 248	31.8	70.0
120 to 125	248 to 257	22.2	51.0
125 to 130	257 to 266	20.4	45.0
130 to 135	266 to 275	18.2	40.0
135 to 140	275 to 284	27.3	60.0
140 to 145	284 to 293	19.1	42.0
145 to 150	293 to 302	21.4	47.0
150 to 155	302 to 311	14.1	31.0
155 to 160	311 to 32-	7.75	17.0
Above 160	Above 320	23.2	51.0
TOTAL		347.45	766.0

Systematic Fractionation

FIRST FRACTIONATION (CURVE 1)—These fractions were then systematically redistilled in the same column. The method employed was to charge the first fraction and distil slowly with a large reflux ratio until the temperature at the top of the column reached the initial temperature of the fraction charged, when the second fraction was charged. The same process was repeated for the latter fractions.

This method gave the more volatile components in a purer state than if the temperature at the top of the column was run up to the initial temperature of the fraction to be charged, as the column would then contain considerable amounts of

the heavier hydrocarbons, which would contaminate the lighter, more volatile hydrocarbons entering the column from the still when the succeeding fraction was charged. Working in this manner, the above fractions were redistilled and the distillate received as shown by Curve 1. In this fractionation the pentane (28° to 38° C.), hexane (60° to 70° C.), and iso-octane (117° to 121° C.) fractions were clearly evident, and there is definite suggestion of isoheptane, heptane, isononane, and nonane.

SECOND FRACTIONATION (CURVE 2)—Those fractions collected at 135° C. (275° F.) or over were then redistilled in the same manner. The distillate was received as shown by Curve 2. The lower boiling fractions were not distilled at this time, as the intent was to work the more volatile components out of the higher boiling fractions.

THIRD FRACTIONATION (CURVE 3)—With the exception of that fraction distilling below 35° C. (95° F.), all fractions were redistilled in the same manner, giving distillate according to Curve 3. The lowest boiling fraction was not run because the losses in distilling material boiling at room temperature are very high. This run shows clearly the presence of the pentanes, hexanes, isoheptane, normal heptane, iso-octane, and normal nonane, while normal octane, two isononanes, and isodecanes are suggested.

FOURTH FRACTIONATION (CURVE 4)—Those fractions collected above 101° C. (214° F.) were then systematically redistilled, giving distillate as shown on Curve 4.

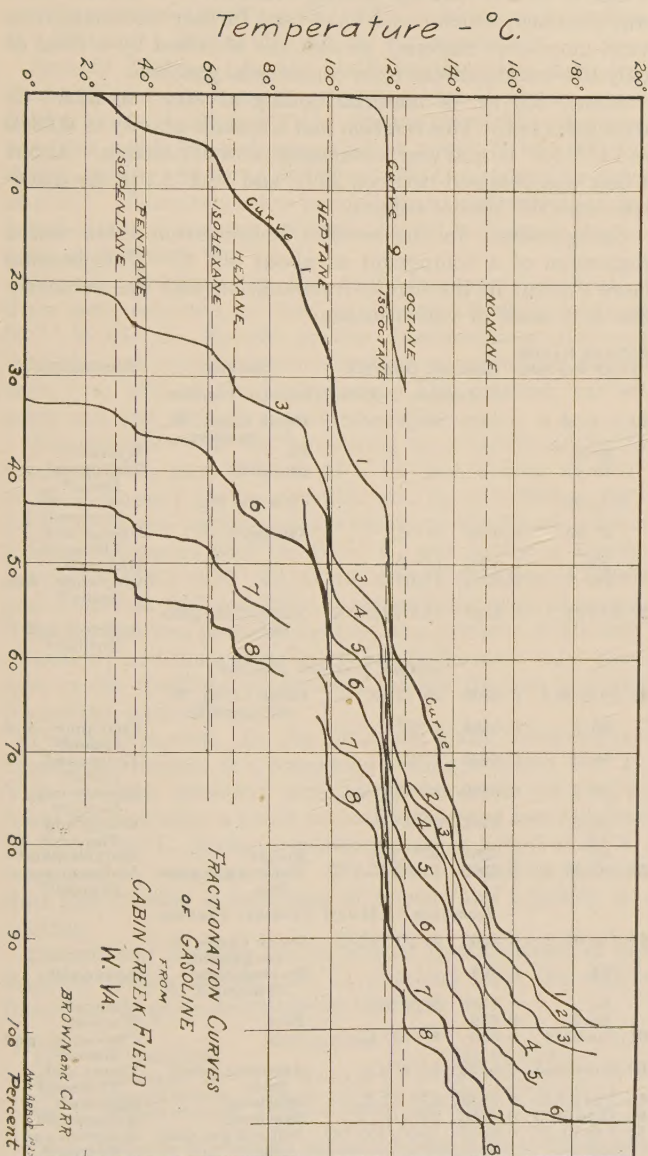
FIFTH FRACTIONATION (CURVE 5)—All fractions collected above 97° C. (207° F.) were then systematically redistilled, giving distillate as shown on Curve 5.

SIXTH FRACTIONATION (CURVE 6)—All fractions were then redistilled, with results as shown by Curve 6. Here the presence of butane was first indicated. The pentane and hexane fractions were beginning each to separate into two fractions and the nonane fractions are clearly defined. The fraction collected under 10° C. (50° F.) was composed largely of butanes and evaporated rapidly, even though kept packed in ice.

As many of the fractions were becoming small in quantity, a fourth column, 10 feet high and 1¼ inches inside diameter, filled with ¼-inch Raschig rings and mounted on a 20-gallon still, was used for the following distillations.

SEVENTH FRACTIONATION (CURVE 7)—The fractions obtained from the sixth fractionation were carefully fractionated with very large reflux ratios, giving the results indicated by Curve 7. The butane came over almost as soon as the lowest boiling fraction had been charged, before any heat was supplied to the still. The temperature indicated was somewhat less than 2° C. (35.6° F.). The isopentane is clearly distinct from the normal pentane fraction and the isohexane is distinct from the normal hexane.

EIGHTH FRACTIONATION (CURVE 8)—*Pentanes*. In the



fifth fractionation of pentanes—carried out in a 2-liter glass still with a 5-foot column packed with $\frac{1}{8}$ -inch rings—200 cc. of isopentane were collected, boiling at 30.5° to 30.6° C. with a specific gravity of 0.6240 at 17°/15.5° C. About a liter of similar material boiling between 29.8° and 30.8° C. was obtained, which could have been further fractionated to yield more pure material, as this was obtained by a total of only five fractionations from commercial gasoline.

About 250 cc. of material boiling at 36.2° to 36.3° C. were collected. This fraction had a specific gravity of 0.6340 at 14°/15.5° C. and was presumably normal pentane. About 1 liter was obtained between 36.0° and 36.4° C. in the distillate from the 10-foot column.

Cyclopentane. In the seventh fractionation there was a suggestion of a component at about 50° C. This became more evident in the eighth fractionation and was evidently due to a trace of cyclopentane.³³

BOILING RANGE ° C. AT 760 MM.	SPECIFIC GRAVITY		SOURCE	REFERENCE
<i>Isopentane (2-Methyl Butane) Fraction</i>				
30.5–to 30.6	0.6220	20°/15.5° C.	Cabin Creek, W. Va. gasoline	Warren ¹⁹
30.2			Pa.	Thorpe and Jones ²⁰
30.4			Synthetic	Mabery and Hudson ²¹
29 to 30			Ohio and Pa.	Young and Thomas ¹⁰
27.95	0.6380	14° C.	Synthetic	Richter ²²
30	0.6385	14° C.		Chavanne and Simon ²³
28	0.6394	4°/0° C.		Anderson and Erskine ¹⁵
27.8 to 28.3	0.6248	15.5°/15.5° C.	Natural gas gaso- line	
<i>Normal Pentane Fraction</i>				
36.2–to 36.3	0.6309	20°/15.5° C.	Cabin Creek, W. Va. gasoline	Chavanne and Simon ²³
36.3	0.6454	4°/0° C.		Thorpe and Jones ²⁰
36.3	0.6475	0° C.		Mabery and Young ²⁴
36.3	0.6250	25°/25° C.		Young and Thomas ¹⁰
36.3	0.6454	0°/4° C.		Markownikoff ²⁵
37	0.6263	17° C.	Russia	Anderson and Erskine ¹⁵
35.5 to 36.0	0.6309	15.5°/15.5° C.	Natural gas gaso- line	
<i>Isohexane (2-Methyl Pentane) Fraction</i>				
61.1 to 61.2	0.6600	20°/15.5° C.	Cabin Creek, W. Va. gasoline	Redwood ²⁸
61	0.664		Pa. and New Brunswick	Mabery ²⁴
61	0.6720	0°/4° C.		Warren ⁹
61.3	0.676		Peru	Chavanne and Simon ²³
61.7 to 62.4	0.658	4°/15° C.		Young and Thomas ¹⁰
60.55 to 60.85	0.6728	0°/4° C.	American petro- leum	Zelinsky ²⁶
60.5 to 61.0	0.6583	17°/4° C.	Synthetic	Rissegem ²⁷
60.15 to 60.2	0.6580	15°/15° C.	Synthetic	Anderson and Erskine ¹⁵
59.7 to 61.0	0.6613	15.5°/15.5° C.	Natural gas gaso- line	Mabery ⁴
61.2	0.6762	0° C.	Ohio and Canada	Thorpe and Jones ²⁰
62	0.6760	0° C.		

Hexanes. About 2 liters of *isohexane*, boiling at 60.5° to 61.5° C. and 5 liters of normal hexane boiling at 68.0°

to 69.0° C. were collected. These fractions were later separately twice fractionated in the 5-foot glass column giving 300 cc. of isohexane boiling at 61.1° to 61.2° C., and having a specific gravity of 0.6620 at 17°/15.5° C., and 1 liter of normal hexane boiling at 68.9° to 69.0° C. and having a specific gravity of 0.6622 at 20°/20° C. and refractive indices of 1.3851 and 1.3840 at 20° and 25° C., respectively.

Benzene Fraction. In the sixth fractionation there was some evidence of a fraction separating from the hexanes and boiling at about 75° to 80° C. During the eighth fractionation this small fraction separated at about 78° to 80° C., with a specific gravity of 0.8590 at 20° C. compared to water at 15.5°. These properties indicate that this fraction is composed partly of benzene and probably an isoheptane or possibly cyclohexane.¹⁸

Heptane Fraction. In the sixth fractionation about 5 liters were collected at 93.8° C. having a boiling range of 93.7° to 94° C. Specific gravity determinations indicated that this cut contained some benzene or naphthene derivatives,¹⁰ as well as the isoheptanes. This fraction was set aside and lost through a leaky container.

The cuts above 95° C., run during the seventh and eighth fractionations, gave 9 liters of a fraction boiling at 98.7° to 99.1° C., and having a specific gravity of 0.7322 at 20°/15.5° C. Upon careful refractionation in the 5-foot column 2 liters boiling at 98.6° to 98.7° C. and having a specific gravity of 0.6893 at 20°/20° C. and refractive indices of 1.4068 and 1.4058 at 20° and 25° C., respectively, were obtained. This product was partially distilled at a pressure of 310 mm. of mercury and the residue had precisely the same vapor pressure as the distillate, indicating that the fraction is a pure compound, normal heptane.

Toluene Fraction. In the fifth and sixth fractionations there was evidence of a compound boiling at about 110° C. This evidence persisted through the seventh and eighth fractionations when a small amount of material was collected at about 110° C. having a specific gravity of 0.8385 at 20° C. compared to water at 15.5° C. These properties indicate that this fraction is composed of toluene and probably isooctanes.

Octanes and Nonanes. Two further fractionations of the material boiling above 115° C. obtained from the eighth fractionation gave the following material:

Volume Cc.	Compound	Boiling range ° C.	Specific gravity
2500	Isooctane	117.9 to 118.1	0.7165 at 20°/4° C.
1100	Normal octane	124.3 to 124.5	0.7262 at 20°/15.5° C.
600	Normal nonane	150.2 to 150.9	0.7380 at 20°/15.5° C.

Curve 9 shows the results on an enlarged scale of the eighth fractionation of isooctane and indicates where the cut was made to obtain material for the final fractionation. The normal octane redistilled in the 5-foot column gave 450 cc. boiling at 124.3° C. with a specific gravity of 0.7123 at 20°/

BOILING RANGE ° C. AT 760 MM.	SPECIFIC GRAVITY		SOURCE	REFERENCE
<i>Normal Hexane Fraction</i>				
68.9 to 69.0	0.6622	20°/20° C.	Cabin Creek, W. Va., gasoline	(Refractive index 1.3851 at 20° C., 1.3840 at 25° C.)
68.95	0.6771	0°/4° C.	Appalachian oil	Mabery ⁴
68.95	0.6770	0°/4° C.	American oil	Young and Thomas ¹⁰
68.5 to 69				Kymer ²⁹
67.9 to 69.2	0.6767	15.5°/15.5°	Natural gas gasoline	Anderson and Erskine ¹⁵
<i>Normal Heptane Fraction</i>				
98.6 to 98.7	0.6893	20°/20° C.	Cabin Creek, W. Va.	(Refractive index 1.4068 at 20° C., 1.4058 at 25° C.)
98.4	0.70186	0°/4° C.	American oil	Young and Erskine ¹⁰
98.25 to 98.45	0.68288	20° C.	Rangoon	Schorlemmer ²
97.5 to 99	0.709	17.5° C.	Peru	Beilstein ³
98.5 to 99.5			American oil	Mabery ⁴
96 to 97			Ohio	Chavanne and Simon ²³
98 to 98.3	0.6879	4°/15° C.		Thorpe ³⁰
98.43	0.70048	0°/4° C.		Anderson and Erskine ¹⁵
98.2 to 99.3	0.7117	15.5°/15.5° C.	Natural gas gasoline	
<i>Isobutane (4-Methyl Heptane) Fraction</i>				
117.9 to 118.1	0.7166	20°/15.5° C.	(Refractive index, 1.40063 at 25° C.)	Cabin Creek gasoline
118	0.7217	(Refractive index, 1.3978 at 23° C.)		Clarke ³¹
<i>Normal Octane Fraction</i>				
124.3 to 124.4	0.7123	20°/20° C.	Cabin Creek (Refractive index 1.4059 at 20° C., 1.4037 at 25° C.)	
124.7	0.7068	15°/15° C.	Sumatra	Clarke ³¹
121	0.732	12.1° C.	American oil	Lemoine ³²
124 to 125	0.7134		Ohio	Mabery and Hudson ²¹
<i>Normal Nonane Fraction</i>				
150.2 to 150.9	0.7380	20°/15.5° C.	Cabin Creek gasoline	
150.8	0.7555		Pa.	Warren ⁹
151			Ohio	Mabery ⁴

20° C., and indices of refraction of 1.4059 and 1.4037 at 20° and 25° C., respectively.

Discussion

Although the fractionating equipment used is not so effective as a properly designed bubble-cap plate column, the results obtained are more satisfactory than any previously reported, and indicate that pure hydrocarbons with boiling points up to 150° C. may be obtained by fractionating commercial petroleum products in efficient columns. For satisfactory results the columns should be well insulated or nearly adiabatic, a large part of the condensate must be returned or refluxed to the top of the column, and distillation must be conducted slowly, with controlled uniform heat input to the still.

In addition to the indication of butane, benzene, cyclopentane, toluene, isooheptane, isononanes, and isodecanes, the products given in the accompanying table were obtained. The thermometer used had been calibrated 4 months pre-

viously by the Bureau of Standards. All temperatures were corrected to 760 mm. mercury pressure. Specific gravities were taken by a calibrated Westphal's balance and are given as taken.

All of these compounds attained by fractionation of gasoline are to a high degree pure.

Acknowledgment

The authors wish to acknowledge the aid of Messrs. Benton, Boiney, Fleming, Hunn, Miles, O'Neil, and Rodenberg in conducting fractionations, and the original suggestion of E. H. Leslie.

Bibliography

- 1—Pelouze and Cahours, *Compt. rend.*, **54**, 1241 (1862); **56**, 505 (1863); **57**, 62 (1863).
- 2—Schorlemmer, *J. Chem. Soc. (London)*, **15**, 419 (1863).
- 3—Beilstein and Kurbatow, *Ber.*, **13**, 2028 (1880).
- 4—Mabery, *Proc. Am. Acad. Arts Sci.*, **31**, 10 (1895).
- 5—Coates and Best, *J. Am. Chem. Soc.*, **25**, 1153 (1903).
- 6—Marcusson, *Mitt. kgl. Materialprüfungsamt*, **31**, 301.
- 7—Mabery, *J. Ind. Eng. Chem.*, **6**, 101 (1914).
- 8—Coates, *J. Am. Chem. Soc.*, **28**, 384 (1906).
- 9—Warren, *Proc. Am. Acad. Arts Sci.*, **27**, 56 (1891); **34**, 92 (1898).
- 10—Young and Thomas, *J. Chem. Soc. (London)*, **71**, 440 (1897); Young, *Ibid.*, **73**, 905, 920 (1898).
- 11—Young, *Chem. News*, **71**, 177 (1895).
- 12—Bushong, *J. Ind. Eng. Chem.*, **6**, 888 (1914).
- 13—Evans, *J. Soc. Chem. Ind.*, **38**, 401T (1919).
- 14—Reed and Williams, *Ibid.*, **38**, 319T (1919); **39**, 289T (1920).
- 15—Anderson and Erskine, *Ind. Eng. Chem.*, **16**, 263 (1924).
- 16—Leslie, "Motor Fuels," **1923**, p. 114. Chemical Catalog Co.
- 17—Dufton, *J. Soc. Chem. Ind.*, **38**, 45T (1919).
- 18—Fortey, *J. Chem. Soc. (London)*, **73**, 932, 949 (1898).
- 19—Warren, *Mem. Am. Acad.*, **9**, 135 (1867).
- 20—Thorpe and Jones, *J. Chem. Soc. (London)*, **63**, 290 (1893).
- 21—Mabery and Hudson, *Proc. Am. Acad. Arts Sci.*, **32**, 101 (1896).
- 22—Richter, "Organische Chemie," 11th ed., **1909**, Aufl. I, p. 90.
- 23—Chavanne and Simon, *Compt. rend.*, **168**, 1324 (1919).
- 24—Mabery and Young, *J. Franklin Inst.*, **162**, 57, 81 (1907).
- 25—Markownikoff, *Ber.*, **30**, 975 (1897).
- 26—Zelinsky, *Ibid.*, **40**, 4743 (1907).
- 27—Risseghem, *Bull. soc. chim. Belg.*, **30**, 8 (1921).
- 28—Redwood, "A Treatise on Petroleum," 3rd ed., **1913**, Vol. I, p. 242.
- 29—Kymer, *J. prakt. Chem.*, **64**, 126.
- 30—Thorpe, *J. Chem. Soc. (London)*, **37**, 73 (1880).
- 31—Clarke, *J. Am. Chem. Soc.*, **33**, 520 (1911).
- 32—Lemoine, *Bull. soc. chim.*, **41**, 163 (1884).
- 33—Young and Richardson, *J. Franklin Inst.*, **47**, 50.

Gaseous Explosions¹

I—Initial Temperature and Rate of Rise of Pressure

By G. G. Brown, E. H. Leslie, and J. V. Hunn

DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF MICHIGAN,
ANN ARBOR, MICH.

The existent literature concerning the effect of initial temperature on gaseous explosions is inconclusive and apparently irreconcilable. Because rate of rise of pressure and rate of combustion are frequently confused with rate of chemical reaction, it is generally assumed that an increase in initial temperature must increase the rate of combustion. Experimental work with a constant-volume bomb demonstrates that an increase in initial temperature above a definite critical value decreases the rate of rise of pressure of a homogeneous gaseous explosion. Theoretical considerations indicate that the existence of such a critical initial temperature is to be expected from our knowledge of gases and gaseous reactions. In mixtures containing an excess of fuel the critical initial temperature is about 75° C. In mixtures containing an excess of air or oxygen the critical temperature has not been noticed in work at room temperature or above.

IN SPITE of the many investigations that have been made concerning the nature of gaseous explosions, the subject offers many fundamental problems for solution. A study of the literature reveals no conclusive evidence of the effect of varying conditions of initial temperature upon the characteristics of gaseous explosions; much of it is conflicting and apparently irreconcilable.

Dixon's² work brought out the fact that an increase in initial temperature from 20° to 100° C. at constant initial pressure decreases the velocity of the detonation wave when "theoretical mixtures" are used.

Nägel³ studied the effect of initial temperature upon the rate of inflammation in the same bomb previously used by Lange,⁴ 40 cm. in diameter and of 33.61 liters capacity. The bomb was immersed in a water bath for temperature control, and equipped with a spark gap located at the center of the sphere. Nägel worked with hydrogen, Dresden city gas (10 per cent CO, 49 per cent H₂, 27 per cent CH₄, 3 per cent

¹ Received January 15, 1925.

² *Trans. Roy. Soc. (London)*, **184A**, 97 (1893).

³ *Mitteilungen über Forschungsarbeiten*, **1908**, Heft 54.

⁴ *Ibid.*, **1908**, Heft 8.

C_2H_4 , 0.3 per cent C_6H_6 , 3 per cent CO_2 , 1 per cent O_2 , 6.7 per cent N_2), and producer gas (18.1 per cent H_2 , 2.2 per cent CH_4 , 0.2 per cent C_2H_4 , 18.9 per cent CO , 0.5 per cent C_6H_6 , 6.9 per cent CO_2 , 0.2 per cent O_2 , 53 per cent N_2). An increase in initial temperature from 15° to 75° C. decreased the rate of rise of pressure upon explosion of a city gas-air mixture containing 8 per cent of gas. At an initial pressure of 0.5 atmosphere a slight increase was noted in one case. With 11 per cent and 16 per cent of gas in city gas-air mixtures an increase in initial temperature to 75° C. increased the rate of rise of pressure in all cases. Nägel's producer gas-air mixtures showed an increase in rate of rise of pressure as the initial temperature was raised to 75° C.

Table I—Effect of Temperature at Constant Pressure on Velocity of Flame Propagation in 12-Inch Bomb⁵

C_2H_2 in air mixture Per cent	Initial temperature ° C.	Average velocity M/sec.
10	25	15
	60	12.2
	70	10.8
	80	10.35
15 }	—	Apparent increase from 25° C. to 75° C. and then a decrease on fur- ther rise to 125° C.
20 }		

Woodbury, Lewis, and Canby⁵ took photographic records of the flame travel in explosive mixtures of acetylene and oxygen with nitrogen in a cylindrical bomb 4 inches in diameter and 12 inches high ignited from the bottom, and on the same time scale recorded the pressure-time curve as indicated by a Midgley pressure element in the upper end of the bomb. They report data showing that initial temperature has a very interesting effect. They found that high initial temperature tends to inhibit the initiation of the detonation wave.

In a written discussion of the paper by Woodbury, Lewis, and Canby,⁵ Dixon⁶ says: "If the initial temperature of the gas is raised 100° C. this rise is not added to the flame temperature." In discussing some pressure time curves of the explosions of petrol-air mixtures obtained by Fenning at the National Physical Laboratory, Ricardo⁷ says: "An increase of 101° C. in the initial temperature means a similar increase in the flame temperature."

Midgley,⁸ Ricardo,⁹ and others¹⁰ found that the engine knock becomes more pronounced as the temperature of the mixture is increased.

⁵ *J. Soc. Automotive Eng.*, **8**, 209 (1921).

⁶ *Ibid.*, **9**, 237 (1921).

⁷ *J. Roy. Aeronaut. Soc.*, **27**, 60 (1924).

⁸ *J. Soc. Automotive Eng.*, **10**, 357 (1922); **12**, 367 (1923).

⁹ *Automobile Eng.*, **11**, 51, 92, 130, 169, 201, 242 (1921); **12**, 265, 299, 329 (1922).

¹⁰ Holloway, Huebotter, and Young, *J. Soc. Automotive Eng.*, **12**, 111 (1923); **14**, 315 (1924); **15**, 255 (1924); Horning, *Automobile Eng.*, **14**, 142 (1924).

Tizard¹¹ suggests that the knock in an internal combustion engine "occurs when the rate of rise of pressure exceeds a certain unknown amount," but regards this suggestion as "a comparatively secondary consideration." He "accepts the view that the rate of combustion increases rapidly with the temperature" and "is led to the conclusion that 'knocking' will occur if, some time before combustion is complete, the whole or part of the gas exceeds a certain temperature," or "if the maximum flame temperature exceeds a certain temperature, which is characteristic of the fuel." This conclusion is based on the assumptions "that the rate of combustion increases rapidly with the temperature" and that rate of combustion is equivalent to rate of pressure rise.

This brief review of the literature shows almost complete disagreement as to the effect of initial temperature upon gaseous combustion. It seems absolutely necessary that the question of the effect of initial temperature upon combustion be settled before gaseous combustion can be understood.

Apparatus

The apparatus as finally developed consists of an explosion bomb, $2\frac{3}{4}$ inches inside diameter and 7 inches long, machined from steel bar stock and assembled with valves and fittings, and pressure indicator with optical system to record the pressure-time curves. The spark plug at the lower right end of the bomb is a porcelain core Champion plug as used on Ford engines. The terminals of the plug are kept at $\frac{1}{32}$ (0.03125) of an inch. The igniting spark is obtained from a Ford spark coil using 7.5 volts on the primary. A standard pressure Bourdon gage is connected to the bomb through a needle valve for the purpose of taking the pressure of the gases in the bomb before and after the explosion. A second needle valve is used to control the admission of gases to the bomb and to remove samples of the gases for analysis.

In the top of the bomb a thermocouple is mounted in a gas-tight joint in such a way that its hot junction is in the approximate center of the combustion chamber. The thermocouple is insulated by winding with asbestos string. The winding of asbestos is overlapped repeatedly to form a nodule, at the desired distance from the hot junction, of sufficient size to fill the gland. This construction is perfectly satisfactory and far superior to any known method of cementing the wires in a gas-tight joint.

The university was in possession of a Midgley indicator¹² which was known to give satisfactory results; and although better adapted for engine work than for individual explosions in a bomb, and by no means gas-tight, this indicator was used for these tests.¹³ Mounted as shown in Figure 1 over a gas-tight copper foil diaphragm, the Midgley indicator

¹¹ *N. E. Coast Inst. Eng. Shipbuilders, Trans.*, **37**, 381 (1921).

¹² Midgley, *J. Soc. Automotive Eng.*, **7**, 491 (1920).

¹³ The authors acknowledge the generous loan of the Midgley indicator by Prof. W. E. Lay, of the Department of Mechanical Engineering.

gave satisfactory results. This construction makes a gas-tight indicator that remains so for twenty-five to fifty explosions unless violent detonation takes place. The pressure adapter allows the use of pistons of varying diameter, and pressures of wide range, without exceeding the limit of the indicator spring.

A 6-volt, 32-c. p. automobile head lamp is used as the light source. In order to record the extremely rapid pres-

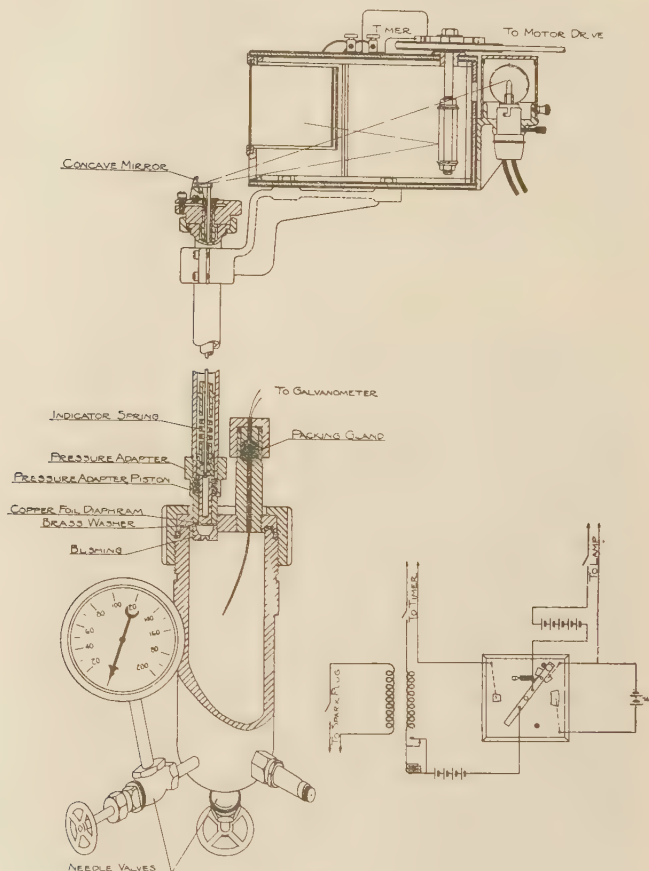


Figure 1—Assembly of Bomb and Indicator

sure rise of detonating explosions, it is necessary to pass 12 volts through the 6-volt lamp during the pressure rise, but the very intense light must be reduced or shut off on the cooling curves to prevent blurring of the curves and destruction of the lamp filament. The lamp control is obtained by a special switch. As the switch handle is manually moved in a clockwise direction 12 volts are passed through the lamp, then the primary circuit of the spark coil is closed, and a spark, properly timed by the timer on top of the camera box and

driven by the shaft of the rotating mirror, ignites the mixture in the bomb. The switch is released and springs back to its original position passing 8 volts through the lamp filament, or it may be moved still further in a clockwise direction, thus breaking the lamp circuit.

Procedure

The fuel used in these experiments was the fraction boiling between 66.9° and 67.4° C. obtained by careful fractionation of a paraffin base gasoline prepared by the Elk Refining Company from crude oil from the Cabin Creek Field, Kanawha Co., W. Va., and was largely isohexane.

Before each experiment the bomb was repeatedly swept out with one of the constituents (nitrogen or oxygen) of the mixture to be exploded. Both valves were closed, the spark plug removed, and the desired amount of hexane immediately introduced into the bomb and spread over the metal surface by means of a small special pipet. The spark plug was replaced and tightened immediately. The desired amount of oxygen and nitrogen, in addition to that already in the bomb, was introduced through the needle valve. The bomb was set in position in the dark room and firmly fastened to the camera box of the Midgley indicator. The gas heater was adjusted to raise the temperature of the mixture in the bomb slowly to the desired temperature as indicated on the galvanometer connected to the thermocouple in the bomb. When the desired temperature and pressure were obtained the gas heater was extinguished, a piece of bromide paper was fastened against the curved glass on the camera box, and the revolving mirror was started. The temperature and pressure of the mixture in the bomb were taken and recorded as the temperature and pressure of the mixture when ignited. The needle valve between the bomb and the pressure gage was closed and the mixture fired at once by means of the switch. The maximum temperature indicated by the thermocouple was recorded, the lamp turned off, and the pressure-time curve developed. The temperature and pressure of the gases within the bomb were then recorded, and the products of combustion analyzed by means of the regular laboratory equipment.¹⁴

Before the experiments were started the pressure element was calibrated by direct dead load, and its calibration was checked against the standard gage at regular intervals.

It may be noticed that some of the pressure-time curves show what appears to be negative time. These peculiar loops can be duplicated exactly in repeated runs and are due to a weakness in the support of the indicator mirror that allows a slight rotation of the mirror in the horizontal plane, when subjected to rapid rotation in the vertical plane.

The pressure is plotted as pressure rise, the zero abscissa representing initial pressure in the bomb. The time is plotted

¹⁴ White, "Gas and Fuel Analysis," 1922. McGraw-Hill Book Co.

with the zero ordinate representing the instant the primary circuit of the spark coil is closed through the switch and timer. There is a limited variable lag between this time and the time the spark ignites the mixture, so that zero time does not represent the instant of ignition with absolute precision. The rate of pressure rise is the most important consideration, and this factor is shown with as much precision as present methods allow.

The numbers in the lower right-hand corners of the graphs represent the test number and are placed there for ease in identification.

Discussion of Results

The results of this investigation of the effect of initial temperature on homogeneous gaseous combustion are in complete agreement with the available record of similar work. Woodbury, Lewis, and Canby⁵ found a slight increase in the rate of flame propagation when rich mixtures—i. e., mixtures containing an excess of fuel—were heated to 75° C. at constant pressure before ignition, and a decrease in the rate of flame propagation as the mixtures were heated above 75° to 125° C. With mixtures containing an excess of oxygen, these investigators found a steady decrease in the rate of flame propagation as the initial temperature was raised at constant pressure from 25° to 80° C. (Table I).

Nägel³ found that an increase in initial temperature from 15° to 75° C. decreased the rate of rise of pressure when a mixture of city gas and air containing an excess of air was exploded at constant initial pressure. In mixtures containing an excess of gas an increase in initial temperature up to 75° C. increased the rate of rise of pressure.

Most of the work of the present investigation on the effect of initial temperature was done under conditions of constant volume or density, because it was considered that the effect of a decrease in density of the charge might obscure the effect of increasing temperature. In fact, the decrease in density was the reason advanced by Dixon² to explain the lower velocity of detonation at 100° C. than at 20° C., and by Woodbury, Lewis, and Canby⁵ to explain the lower rate of flame propagation at higher temperatures.

In the case of mixtures containing an excess of fuel there is a critical temperature, about 75° C., which must be exceeded before the retarding influence of increasing initial temperature is noticed. Below this critical initial temperature an increase in temperature increases to a limited extent the rate of rise of pressure and combustion. In mixtures containing an excess of oxygen this critical temperature has not been noticed in work conducted at room temperature or above. In every case an increase in the initial temperature of the explosive mixture, above 75° C., decreased the rate of pressure rise.

These definite results, taken with the limited data given by Woodbury,⁵ are direct evidence that a critical initial tem-

Table II.—Test Data

Mixture Plate	$C_8H_{18} + 6 O_2 + 3 N_2$						$C_8H_{18} + 6.9 O_2$						$C_8H_{18} + 7.1 O_2 + 5.15 N_2$						$C_8H_{18} + 8 O_2 + 14 N_2$					
	I			II			III			IV			V			VI			VII			VIII		
Figure	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
Test	54	51	52	1064	1091	1025	1032	1030	1023	1033	1025	1023	1033	1025	1023	1033	1025	1023	1033	1025	1023	1033	1025	1023
Initial temperature, ° C.	60	75	80	20	187	152	20	72.5	152	25	150	150	20	72.5	152	25	150	150	20	72.5	152	25	150	150
Initial pressure, lbs./sq. in.	34	34	37	Atmos.	8	32	20	23.3	32	40	67.5	67.5	20	23.3	32	40	67.5	67.5	20	23.3	32	40	67.5	67.5
Average rate of rise of pressure, lbs./sq. in./sec.	430,000	600,000	300,000	530,000	69,000	230,000	455,000	138,000	47,500	32,800	32,800	32,800	47,500	138,000	47,500	32,800	32,800	32,800	47,500	138,000	47,500	32,800	32,800	32,800
Combustion	Click	Click	Click	Click	Quiet	Click	Click	Click	Click	Click	Click	Click	Click	Click	Click	Click	Click	Click	Click	Click	Click	Click	Click	Click
Final pressure at initial temp. lbs./sq. in. gage	27	35	35	...	12	11	20	20	31	36	61	61	20	23.3	32	40	67.5	67.5	20	23.3	32	40	67.5	67.5

Products of combustion:

CO_2	16.9	21.25	20.4	32.5	48.8	46.0	44.0	39.9	23.4	23.7
C_2H_4	0.2	0.55	0.2	...	0.5	+0.0	0.1	0.0	0.2	0.0
O_2	1.0	0.6	2.1	3.9	2.2	2.6	1.8	1.4	2.6	2.0
CO	22.6	20.9	19.6	24	24.8	2.2	6.2	7.9	0.2	0.0
CH_4	...	...	...	...	3.15*	...	...	...	...	...
H_2	...	...	...	...	14.9	...	...	...	...	...
N_2	...	...	...	...	5.5	...	...	...	...	...

Soot deposited.
Same charge
ignited spontaneously
at 200° C.

perature giving a maximum rate of pressure rise exists in explosive gases. It must be admitted that an increase in initial temperature above a definite critical point decreases the rate of rise of pressure even when the initial pressure is increased so as to maintain the density of the charge.

It is common experience that an increase in temperature invariably increases the rate of chemical action. Because combustion is a chemical reaction it is apparently reasonable to expect that the rate of gaseous combustion must be in-

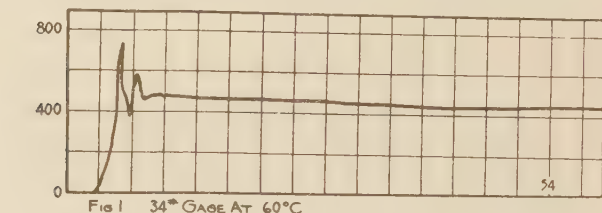


FIG 1 34° GAGE AT 60°C

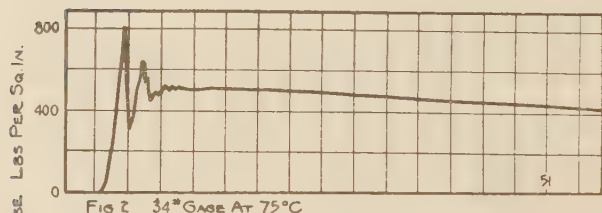


FIG 2 34° GAGE AT 75°C

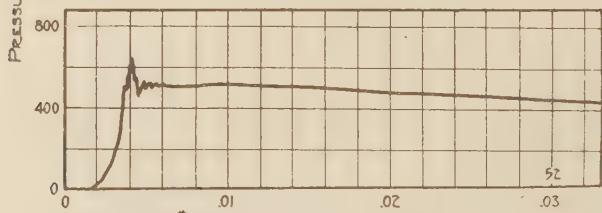


FIG 3 39° GAGE AT 80°C
 $C_6H_{14} + 6O_2 + 3N_2$ INCREASING TEMPERATURE AT CONSTANT PRESSURE

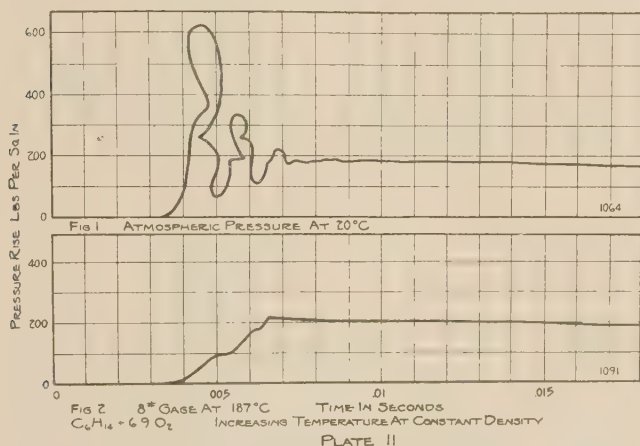
PLATE I

creased by an increase in temperature. This is no doubt true where the gases are passed through a hot zone which serves to ignite the succeeding layers of gas, as is the case of furnaces, surface combustion, ammonia oxidation, and similar processes. But in combustion in a closed vessel where the gases are ignited at one point only, it becomes necessary for each succeeding layer of gas to be ignited by the adjacent burning layer. Under these conditions the rate of inflammation (spread of flame) is limited by the rate at which a burning layer of gas will ignite the adjacent unburnt layer, and this rate may be quite different from the rate of chemical action.

Also, the rate of rise of pressure is not the same as the rate of combustion or even of inflammation.¹⁵ The precise distinction between rate of pressure rise, rate of flame travel, rate of chemical reaction, and rate of combustion may be difficult, but is absolutely necessary if accurate assumptions are to be made. The subject is admittedly complicated and can best be attacked by making no unnecessary assumptions as to the mechanism of combustion, but by applying only those fundamental laws of thermodynamics that are applicable to any isolated system.

Theoretical Considerations

When stagnant gaseous explosive mixtures are ignited in a constant-volume bomb at the same temperature as the gaseous mixture, by an electric spark, the resulting explosion takes place in the gas phase and is a homogeneous reaction. The following theoretical considerations of a qualitative nature



show that a critical initial temperature giving a maximum rate of rise of pressure is to be expected from our knowledge of gases and chemical reactions.

EFFECT OF INITIAL TEMPERATURE, PER SE, UPON PRESSURE RISE—If a volume of gas at 300° K. (absolute) is heated sufficiently to raise its temperature 300° C. to 600° K. (absolute), its absolute initial pressure is doubled. If the gas is initially at 900° K. and its temperature is raised 300° C. to 1200° K., the absolute initial pressure is increased only one-third. If the gases in each case are at the same initial pressure the ratio of pressure rise is 3:1.

Expressed in terms of the gas laws,

$$PV = NRT \quad (1)$$

where P = absolute pressure of gas within the bomb
 V = volume of contents of the bomb
 T = absolute temperature of gas in the bomb
 R = a constant

¹⁵ Hopkinson, *Proc. Roy. Soc. (London)*, **77A**, 387 (1906).

Concerning the magnitude of the pressure rise when the charge is heated at constant volume with no change in the number of molecules,

$$\begin{aligned}\int V dP &= \int N R dT \\ \int dP &= \int \frac{N R}{V} dT \\ \Delta P &= \frac{N R}{V} \Delta T \\ \Delta P &= \frac{P}{T} \Delta T\end{aligned}\tag{2}$$

where d = differential or infinitesimal increment
 Δ = finite increment or change

Equation 2 indicates that the increase in pressure varies directly with the initial pressure and temperature rise, but inversely as the initial temperature. These facts have been well known to engineers for some time.¹⁶

When an explosive mixture is ignited under these conditions the temperature rise (ΔT) is determined by dividing the amount of heat supplied to the gases in the bomb during the explosion (Q) by the specific heat of the combustion products (C_v).

$$\Delta T = \frac{Q}{C_v}\tag{3}$$

$$\Delta P = \frac{P}{T} \frac{Q}{C_v}\tag{4}$$

This equation may be used to explain in a precise manner many facts that are frequently misstated. It is generally stated that a greater pressure rise is obtained with a cooler charge because a greater weight of mixture has been taken into the cylinder. This is not an accurate statement; the greater weight of charge does not increase the initial pressure, or the rise in temperature, because the increase in heat liberated (Q) is absorbed by the equivalent increase in specific heat (C_v). A cooler mixture gives a greater pressure rise because it is at a lower temperature.

Concerning the rate of rise of pressure (dP/dt), by a similar process,

$$\frac{dP}{dt} = \frac{P}{T C_v} \frac{dQ}{dt}\tag{5}$$

where t = time

Under actual conditions, as the specific heat (C_v) increases with temperature, more heat is required to raise the temperature from 900° to 1200° K. than from 300° to 600° K., and heat would have to be supplied more than three times as fast to a gas volume at 900° K. than at 300° K. to give the same rate of rise of pressure.

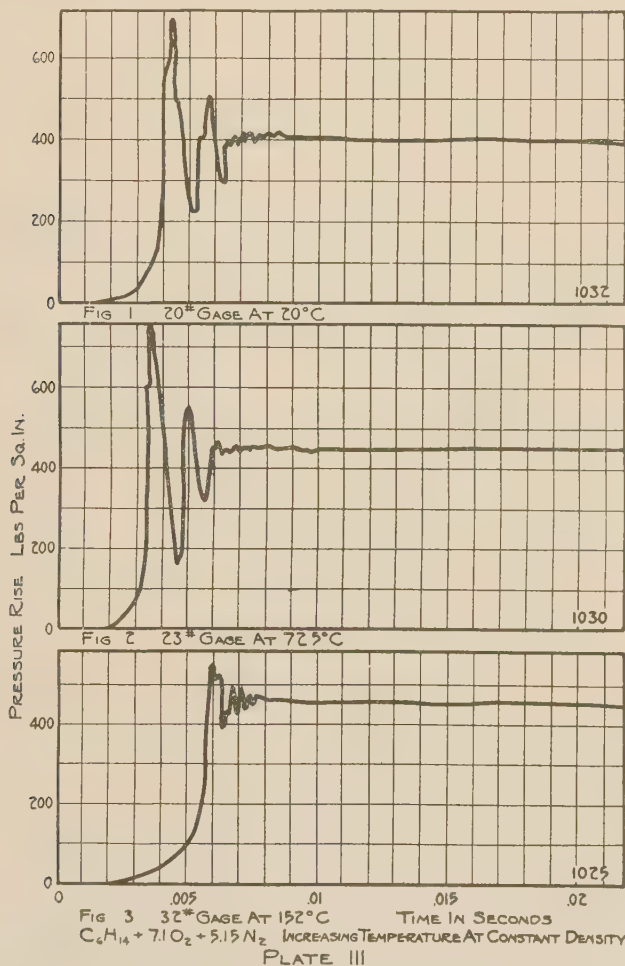
¹⁶ Clerk, "Gas, Petrol, and Oil Engines," 1909. John Wiley & Sons., Inc.

$$\frac{dQ}{dt} = h k \quad (6)$$

h = heat of molecular reaction
 k = reaction velocity expressed in number of mols per mol of fuel per unit of time

$$\frac{dP}{dt} = \frac{P h k}{T C_p} \quad (7)$$

Equation 7 makes clear the distinction between rate of rise of pressure (dP/dt) and rate of reaction (k). The rate



of rise of pressure varies inversely as the initial temperature and directly as the rate of chemical reaction (k), which in turn varies directly as the temperature. It is therefore evident that the reaction velocity (k) cannot be substituted for rate of rise of pressure, as some writers have done.

EFFECT OF INITIAL TEMPERATURE UPON RATE OF REACTION—An increase in temperature increases the velocity of a chemical reaction, but an increase in temperature at constant pressure decreases the density or concentration. Therefore, the effect of increasing the initial temperature at constant pressure upon reaction velocity is twofold, one directly increasing the rate of reaction and the other tending to decrease the rate of reaction if above the first order.

From the following equation due to van't Hoff,¹⁷

$$\frac{d \log_e k}{dT} = \frac{B}{T^2} \quad (8)$$

where k = reaction velocity
 B = a constant

an expression for k as a function of T may be obtained

$$\log_e k = -\frac{B}{T} + C'$$

$$k = C'' e^{-\frac{B}{T}} \quad (9)$$

For a gaseous mixture of given composition at constant temperature,

$$k = C''' D^{(a-1)} \quad (10)$$

where k = reaction velocity
 C''' a constant
 D = density
 a = order of reaction—i. e., the number of molecules entering into reaction

Combining Equations 9 and 10,

$$k = C'D^{(a-1)} e^{-\frac{B}{T}} \quad (11)$$

For a gaseous reaction

$$D = C'' \left(\frac{P}{T} \right) \quad (12)$$

Combining Equations 11 and 12

$$k = C \left(\frac{P}{T} \right)^{(a-1)} e^{-\frac{B}{T}} \quad (13)$$

At constant pressure and composition k varies as

$$\frac{e^{-\frac{B}{T}}}{T^{(a-1)}}$$

This expression has a maximum value when $T = \frac{B}{a-1}$. As B is always positive and a is always a positive integer not less than 1, the velocity of reaction k is a maximum for a given initial pressure at some finite positive temperature when the order of the reaction is greater than 1.

If the reaction is of the first order, or the initial density of the gaseous mixture is the same, the rate of reaction increases

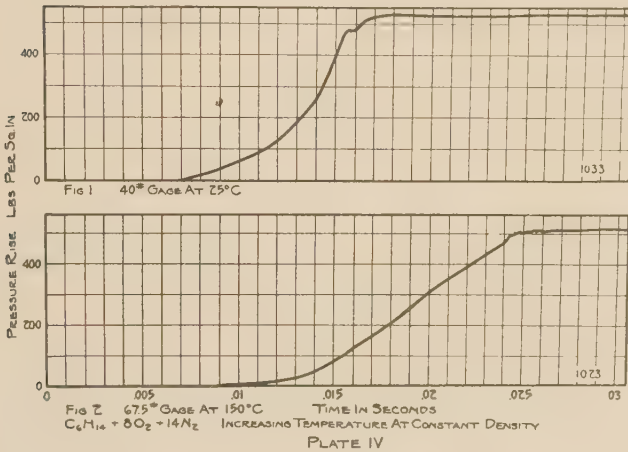
¹⁷ Nernst, "Theoretical Chemistry," 1911, Macmillan Co.; Washburn, "Principles of Physical Chemistry," McGraw-Hill Book Co.

without limit as the initial temperature is increased. Under these same conditions the rate of rise of pressure has been shown to decrease as the initial temperature was increased beyond a limit (about 75° C.).

EFFECT OF INITIAL TEMPERATURE ON RATE OF RISE OF PRESSURE—By combining Equations 7 and 13 an expression for the rate of rise of pressure of a gaseous explosion at constant volume as a function of initial temperature and pressure is obtained.

$$\frac{dP}{dt} = C \times \frac{h}{C_v} \times \left(\frac{P}{T}\right)^a \times e^{-\frac{B}{T}} \quad (14)$$

If it is assumed that $\frac{h}{C_v}$ is constant, the rate of rise of



pressure (dP/dt) is a maximum for a given mixture at a given initial pressure when $\frac{e^{-\frac{B}{T}}}{T^a}$ is a maximum or $T = \frac{B}{a}$

As B and a are always positive and finite it is evident that the initial temperature (T) has a positive finite value for maximum rate of rise of pressure under these conditions.

With all actual gases C_v is not constant but increases with the temperature. For the present qualitative discussion the specific heat of the products of combustion may be represented by the following expression:

$$C_v = b + cT$$

where b and c are positive constants

Substituting this expression for C_v in Equation 14,

$$\frac{dP}{dt} = \frac{C \times h}{(b + cT)} \left(\frac{P}{T}\right)^a e^{-\frac{B}{T}} \quad (15)$$

(13)

For maximum dP/dt at constant initial pressure (P)

$$d \left[\frac{e^{-\frac{B}{T}}}{(b + cT)T^a} \right] = 0$$

$$\frac{B}{T^2} - \frac{a}{T} - \frac{c}{b + cT} = 0$$

$$T = - \frac{(ab - Bc) \pm \sqrt{(ab - Bc)^2 + 4bBc(a + 1)}}{2c(a + 1)}$$

As all these constants, a , b , c , and B , are positive and finite, the initial temperature (T) has a real positive value for the maximum rate of rise of pressure of an explosive mixture at a given initial pressure.

In considering the case of constant initial density of the explosive mixture, P/T is constant and the expression is simpler. For maximum dP/dt from Equation 15,

$$d \left(\frac{e^{-\frac{B}{T}}}{b + cT} \right) = 0$$

$$T = \frac{+B \pm \sqrt{B^2 + 4bB/c}}{2}$$

As b , c , and B are positive and finite, the initial temperature (T) has a real positive value for the maximum rate of rise of pressure for a given density of an explosive mixture.

Conclusion

Because rate of rise of pressure and rate of combustion have been confused with rate of reaction, it has generally been assumed that an increase in initial temperature must increase the rate of combustion or of rise of pressure of a gaseous explosion. The experimental work reported in this paper shows that an increase in initial temperature above a definite critical value decreases the rate of rise of pressure of a gaseous explosion. The theoretical considerations presented show that the existence of a critical initial temperature is to be expected from our knowledge of gases and gaseous reactions.

Gaseous Explosions

II—Homogeneous and Heterogeneous Reactions Defined and Classified

By George Granger Brown

UNIVERSITY OF MICHIGAN, ANN ARBOR, MICH.

Gaseous reactions may be divided into two classes, homogeneous reactions wholly confined to a single gas phase and heterogeneous reactions occurring at the interface between two phases. Homogeneous reactions are continuously homogeneous if all parts of the gas phase are in the same stage of reaction at the same time, progressive homogeneous reactions if the zone of reaction advances continuously through the gas, or hetero-homogeneous if indirectly modified by another phase. Heterogeneous reactions are gas-gas if the reaction occurs at the interface between two gas phases, gas-liquid if the reaction occurs at the interface between a gas phase and a liquid phase, or gas-solid if the reaction occurs at the interface between a gas phase and a solid phase.

THE properties of gaseous reactions and explosions occurring under different conditions vary in an apparently inconsistent manner. In a previous paper¹ the conflicting evidence concerning the effect of initial temperature upon the rate of rise of pressure of a gaseous explosion was briefly reviewed, and all the apparently conflicting evidence obtained from experimental work with quiet mixtures in a bomb was reconciled by the recognition of the fact that there is a critical initial temperature that gives the maximum rate of rise of pressure in a homogeneous gaseous explosion. In internal combustion engines conditions are such that an increase in initial temperature usually increases the rate of rise of pressure. There is also evidence that the rate of rise of pressure on ignition may increase as the initial temperature is lowered in cold engines.

Throughout this discussion a gaseous explosion means a sudden rise in pressure due to exothermal gaseous reaction, as distinct from a sudden fall in pressure as of an "exploding" steam boiler. Such explosions are of great practical importance, particularly in internal combustion engines. Because of the complicated nature of these reactions and the large number of variables that must be considered, workers in this field find it difficult to meet on a common ground and make many conflicting statements of fact as well as theory. If these reactions can be definitely classified and the properties

¹ Brown, Leslie, and Hunn, *THIS JOURNAL*, **17**, 397 (1925).

of the different types studied, order may be brought out of the present chaos.

Gaseous reactions are susceptible to a natural classification that brings reactions with the same properties into the same class and eliminates from that class other reactions of distinctly different properties. A careful review of the known properties of gaseous reactions indicates that such reactions are no exception to the major classification generally adopted for all chemical reactions. This classification into homogeneous and heterogeneous reactions has been found to aid greatly in a systematic study of this subject.

Exactly where to draw the line between homogeneous and heterogeneous gas reactions is not obvious, and such distinction can be made only upon the basis of some clear-cut, easily defined classification.

Homogeneous Reactions

A homogeneous reaction is a reaction wholly confined to a single phase,² which must be homogeneous before and after the reaction, although not necessarily completely homogeneous while the reaction is taking place. A phase is any homogeneous part of a system, bounded by a surface and mechanically separable from the other parts of the system. "Such a phase is necessarily in one of the three physical states of aggregation, gaseous, liquid, or solid."²

It does not necessarily follow that a reaction between gases is a homogeneous reaction because a gaseous phase is a homogeneous part of a system. A gaseous reaction is a homogeneous reaction only when the reaction is wholly confined to a single gas phase, and independent of the condition or extent of the surfaces or phases bounding this gas phase. If these surfaces have any direct effect on the reaction, other than to limit the extent of the gas phase, the reaction is not wholly confined to a single phase and cannot be classed as a homogeneous reaction. But the fact that the surfaces limit the extent of the gas phase even in a homogeneous reaction accounts for an indirect effect of the bounding surfaces on a reaction wholly confined to a single gas phase. This type of reaction is discussed as a hetero-homogeneous reaction.

Even among those reactions that are wholly confined to a single phase, at least three different types of homogeneous reactions can be recognized.

(1) *Continuously Homogeneous Reactions*

Reactions occurring entirely within a gas phase, all parts of the gas phase in the same stage or degree of completeness of reaction at the same instant so that the gas phase is completely homogeneous throughout the course of the reaction, may be considered continuously homogeneous reactions, or homogeneous reactions of the first class.

This type of reaction is identical with the usual homo-

² Hill in, "A Treatise on Physical Chemistry," edited by Taylor, pp. 343 and 370. D. Van Nostrand Co., New York.

geneous reaction that takes place in liquid solution, and is represented in the gaseous phase by reactions such as the decomposition of sulfuryl chloride into sulfur dioxide and chlorine³ in glass at 320° C. and the decomposition of nitrogen pentoxide into nitrogen tetroxide and oxygen.⁴ Such reactions represent a uniform approach to equilibrium as conditions are changed, and are never the major reactions in a gaseous explosion.

(2) Progressive Homogeneous Reactions

A homogeneous mixture of hydrogen and oxygen at room temperature is not at equilibrium. A slow oxidation of the hydrogen is taking place under these conditions. This slow, uncatalyzed oxidation is a continuously homogeneous reaction of the type described above.

If the rate of reaction between the hydrogen and oxygen of this mixture is increased by any means so that the hydrogen burns, a flame appears at some point in the mixture and very rapidly spreads throughout the entire mixture causing an explosion. No matter how this explosive mixture is ignited, it seems impossible to cause complete instantaneous inflammation; the flame always first appears at some point in the mixture and spreads more or less rapidly, depending upon conditions. This explosive reaction occurs entirely within a gas phase, but all parts of the gas are not in the same stage of reaction at the same instant as the zone of reaction advances continuously through the gas.

Although all parts of the gas mixture are not homogeneous during inflammation, the reaction is essentially a continuous succession of reactions that are locally homogeneous. This may be made clear by considering a cylinder of gas divided into very thin layers as shown in cross section in Figure 1-A. When the first layer is ignited it bursts into flame, expands, and compresses the unburned gases in layers 2, 3, 4, etc., as shown

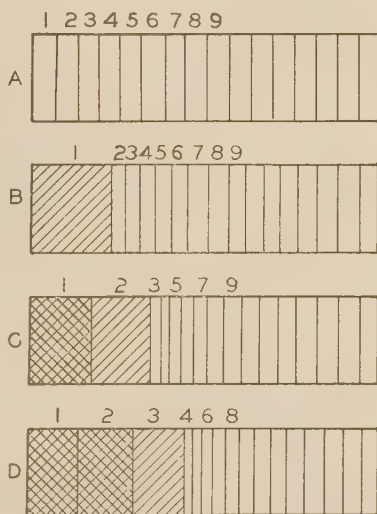


Figure 1—Progressive Homogeneous Reaction

in B. The second layer of gas, ignited and inflamed as the flame advances through the gaseous mixture, expands and compresses the unburned gas in layers 3, 4, 5, etc., and

³ Smith, *J. Am. Chem. Soc.*, **47**, 1862 (1925).

⁴ White and Tolman, *Ibid.*, **47**, 1240 (1925).

the burned gas in layer 1. The combustion of the gas in layer 2 takes place under different conditions than the combustion of layer 1, and layer 3 burns under still different conditions, as do all the succeeding layers.

This reaction differs from a continuously homogeneous reaction in two important respects. Each succeeding layer of gas is burned later and ordinarily under different conditions, instead of at the same time and under the same conditions. It is similar to a continuously homogeneous reaction in being entirely independent of the surface of the container, and, if we consider each layer of gas an infinitesimal layer, is essentially a continuous succession of different continuously homogeneous reactions. For these reasons a reaction occurring entirely within a gas phase, the zone of reaction advancing through the gas in the manner described, is considered a progressive homogeneous reaction, or homogeneous reaction of the second class.

(3) *Hetero-homogeneous Reaction or Compound Progressive Homogeneous Reaction*

A reaction wholly confined to a single gaseous phase must be a homogeneous reaction by definition. But if the reaction is greatly influenced and its properties modified by the surface bounding the gas phase, although the reaction does not occur at these surfaces, the reaction is not a simple homogeneous reaction of either class (1) or (2), but a complex homogeneous reaction defined as a "hetero-homogeneous reaction" because it is wholly confined to a single gas phase but partially determined or influenced by the surfaces of another phase (or phases) bounding the gas phase.

Mallard and LeChatelier⁵ photographed the flame passing through an explosive mixture along a horizontal tube, on photographic paper moving vertically. These photographs show three distinct stages of flame propagation in homogeneous gaseous explosions in a closed tube, and only two stages in those explosions fired near the closed end of a tube open at the far end. These stages are as follows:

1—Initial accelerating continuous propagation (a progressive homogeneous reaction).

2—Vibratory movement which either extinguishes the flame or develops into the third stage (a hetero-homogeneous reaction).

Note—This stage is never observed in mixtures fired near the closed end of a tube open at the far end; the flame is then uniformly accelerated until the detonation wave is developed.

3—Detonation wave. A very rapid, intensely luminous high pressure wave propagated at a constant velocity that is independent of the material or diameter of the combustion tube, but determined by the conditions of the experiment.⁶ (A progressive homogeneous reaction.)

⁵ *Ann. mines*, [8] 4, 274 (1883); *Ann. chim. phys.*, [5] 28, 289 (1883); *Compt. rend.*, 91, 825 (1880); 93, 145 (1881); 95, 566 (1882).

⁶ Berthelot, *Ibid.*, 93, 18 (1881).

The fact that the vibratory stage in a homogeneous gaseous explosion is evident only when the far end of the tube is closed, is direct evidence that this vibratory stage is dependent upon the surface bounding the gas phase at the far end. Dixon⁷ has demonstrated that a pressure wave resembling a sound wave is initiated when an explosive mixture is ignited and that this pressure wave reflected from the far end of the tube has a pronounced effect upon the combustion and flame propagation in the explosive mixture. In a tube closed at both ends and containing an explosive mixture of $2\text{H}_2 + \text{O}_2$ ignited at the center, these pressure waves are reflected back and forth throughout the length of the tube, causing the

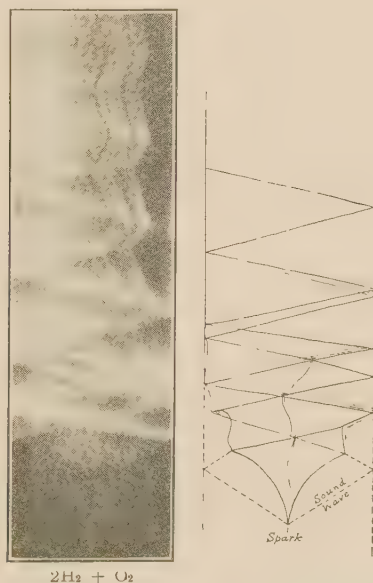


Figure 2—Photograph and Interpretation of Movements of Gas Particles during Combustion

The explosion occurred in a horizontal tube closed at both ends. The mixture ($2\text{H}_2 + \text{O}_2$) was ignited in the center of the tube and the photographic film was moved vertically downward across the horizontal window in the tube.

vibratory movement of the flame as shown in the photograph of Figure 2.⁸ In addition to the vibratory movement, Dixon's work shows that these pressure waves have an accelerating or intensifying effect upon the combustion because of the greater concentration of the gas in the pressure wave. This can be seen clearly in the photograph.

Not only do these pressure waves in an explosive mixture modify or intensify the combustion taking place, but the pres-

⁷ *Trans. Roy. Soc. London*, **200A**, 319 (1903).

⁸ *J. Soc. Automotive Eng.*, **9**, 237 (1921).

sure waves may ignite the unburned gas ahead of the flame by adiabatic compression in much the same way that a detonator cap sets off the main charge of a solid explosive. This "auto-ignition" of the explosive mixture ahead of the flame occurs probably where the pressure wave is reflected from some solid surface or where two pressure waves meet, because then the intensity of the adiabatic compression is the sum of the two compressions in the two waves or in the wave and the reflected wave. Dixon⁸ has published a photograph showing the movements of the flame in a mixture of hydrogen with three volumes of oxygen fired by a spark near the right side of the tube while the gases were being compressed by the sudden thrust of a piston from the left. At the moment the spark was passed the gas had been compressed to one-quarter of its original volume. The pressure wave started by the initiation of the explosion reached the advancing face of the piston before the flame, ignited the gas at the face of the piston, and on reflection checked the advance of the flame, initiated by the spark.

In this case the reaction or explosion is entirely confined to the gas phase and is therefore a homogeneous reaction; but because the double ignition (auto-ignition) developed by the pressure wave was dependent upon this pressure wave being reflected by the surface bounding the gas phase, the reaction is not entirely independent of the bounding surfaces and is defined as a hetero-homogeneous reaction.

Further evidence^{9,10} of these types of reactions is so complete that this classification of homogeneous gaseous reactions is presented without further qualifications.

Heterogeneous Reactions

A heterogeneous reaction is a reaction occurring at the interface between two phases. Any reaction dependent upon two substances not contained in a single homogeneous phase coming into contact can occur only at the interface between the two phases and is a heterogeneous reaction.

In general, heterogeneous reactions are classified according to the phases involved.

(1) Gas-Gas Heterogeneous Reaction

A gas-gas reaction is a reaction occurring at the interface of two gaseous phases. It has generally been assumed that but one gas phase can be present if no restraining containers are used to separate the gases. This assumption, fully justified for systems at equilibrium, is not always true under actual conditions, which may be far from equilibrium.

If city gas is allowed to escape from a gas cock into the

⁸ Foley and Souder, *Phys. Rev.*, **35**, 373 (1912), present photographs actually showing the sound or pressure wave advancing from the spark through the explosive mixture ahead of the flame and hot gases, and the reflection of these pressure waves from the walls of the container.

¹⁰ Woodbury, Lewis, and Canby, *J. Soc. Automotive Eng.*, **8**, 209 (1921); Bradshaw, *Proc. Roy. Soc. London*, **79A**, 236 (1907); Ellis and Wheeler, *Fuel*, **4**, 356 (1925).

air and the gas is ignited, the combustion, which can occur only when gas and air come into contact, obeys all the laws of a heterogeneous reaction. In this case the velocity of the reaction depends upon the rate of diffusion of the air and gas to the interface and upon the rate of diffusion of the combustion products away from the interface, as well as upon the rate of chemical reaction in the interface. If the gas is emitted with a higher velocity, introducing turbulence and eddy currents into the flow stream, the rate of combustion is increased because the rates of mixing are increased. This principle is recognized and widely used by combustion engineers.

A gas-gas heterogeneous reaction may be of importance in gaseous explosions. In internal combustion engines this type of reaction might be expected in engines using a stratified charge, and in the fuel injection engines such as those working on the Diesel cycle, in which the air used for combustion is compressed to a high pressure and temperature in the engine cylinder and the fuel subsequently injected, vaporized, and burned during the power stroke. A high degree of turbulence, however, causes such intimate mixing that the gas-gas heterogeneous reaction rapidly approaches homogeneous reaction as the rates of mixing exceed the rate of a homogeneous chemical reaction.

(2) *Gas-Liquid Heterogeneous Reaction*

A gas-liquid reaction is a reaction occurring at the interface of gaseous and liquid phases.

In general, the same statement may apply to gas-liquid reactions as was made concerning gas-gas heterogeneous reactions. In fact, evidence indicates that liquids are vaporized before oxidation takes place in most combustion reactions. Whether or not this is always true is probably of no importance, as in either case the reaction is a surface or heterogeneous reaction and therefore governed by the same laws. It is well-known that oil fuel may be burned more quickly and completely if finely atomized and injected with turbulent flow into the furnace or engine than if introduced as a viscous stream.

If the liquid is uniformly distributed throughout the mixture in the form of a fine mist, the explosive reaction takes place in a mixture that may be considered essentially homogeneous and the reaction approaches a homogeneous reaction. This statement is directly supported by the work of Haber and Wolff,¹¹ who found that the properties of an explosion occurring in a fuel-mist air mixture are similar to the properties of a progressive homogeneous gaseous explosion.

(3) *Gas-Solid Heterogeneous Reaction*

A gas-solid reaction is a reaction occurring at the interface of gaseous and solid phases.

¹¹ *Z. angew. Chem.*, **36**, 373 (1923).

In addition to reactions between gases and solids as dust explosions and explosions in a coal calorimeter bomb, the catalytic action of solid surfaces on explosions of gaseous mixtures is extremely important.¹² Many reactions between gases are greatly catalyzed by solid surfaces, particularly when the surfaces are heated to high temperatures. The so-called "surface combustion" furnace is the extreme application of this principle to industrial furnaces.

Many investigators have emphasized the important effect of hot surfaces on the combustion of explosive mixtures in internal combustion engines. In general, the engine knock in a high-compression, multiple-cylinder engine may be largely stopped by properly cooling the suspected high-temperature areas.¹³ As the exhaust valve is probably the most highly heated area within the combustion chamber, proper cooling of the exhaust valve or its complete elimination makes more difference than any other surface factor.¹⁴

Catalysis

Midgley and Boyd¹⁵ have shown that catalysts mixed with the liquid fuel used in internal combustion engines have very important effects on the explosion. These catalysts become intimately mixed with the fuel and uniformly distributed throughout the explosive mixture as vapor or at least as a fine mist. In this condition as a part of the homogeneous mixture these catalysts influence all homogeneous reactions as well as heterogeneous reactions involving the explosive mixture.

Surface catalysis of gaseous reactions makes the reaction heterogeneous. For this reason all gaseous reactions catalyzed by surfaces are included under heterogeneous reactions. As a large number of gaseous reactions are subject to contact catalysis, catalytic heterogeneous gaseous explosions are very important, particularly in internal combustion engines.

¹² Sokal, *J. Soc. Chem. Ind.*, **43**, 283T (1924).

¹³ Holloway, Huebotter, and Young, *J. Soc. Automotive Eng.*, **12**, 111 (1923); Young and Holloway, *Ibid.*, **14**, 315 (1924); **15**, 255 (1924); Horning, *J. Soc. Automobile Eng.*, **14**, 142 (1924).

¹⁴ Abell, *J. Soc. Automotive Eng.*, **13**, 301 (1923).

¹⁵ *THIS JOURNAL*, **14**, 894 (1922).

